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by Edgar L. Wong, Andrew E. Potter, Jr., and Frank E. Belles

Lewis Research Center
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SUMMARY

A mass spectrometer stirred reactor technique was used to measure the rates of reaction of carbon monoxide with hydroxyl radicals and with oxygen atoms ($CO + OH \rightarrow CO_2 + H$ and $CO + O + M \rightarrow CO_2 + M$).

For the $CO + OH \rightarrow CO_2 + H$ reaction in the temperature range of 310° to 611° K, the rate constant based on CO_2 production was $4.2 \pm 0.8 \times 10^{11} \exp(-1200 \pm 300/RT)$ cubic centimeters per mole per second, where R is the gas constant and T is the absolute temperature. The rate near room temperature is lower than other values reported recently. The activation energy of 1200 calories per mole (5000 J/mole) is in good agreement with recent estimates.

For the $CO + O + M \rightarrow CO_2 + M$ reaction, an upper limit value for its rate constant based on CO_2 production was estimated to be 4×10^{13} cubic centimeters squared per mole squared per second at 500° K.

Since the CO + OH reaction is considerably faster than the CO + O + M reaction, trace impurities giving rise to OH interfere with CO + O + M rate measurements, and may be responsible for the large differences in rate constants reported by various investigators for this reaction.

INTRODUCTION

The oxidation of carbon monoxide to carbon dioxide is an important process in combustion and in the photochemistry of CO_2. This oxidation process is catalyzed by traces of hydrogen or hydrogen-containing compounds. The effect is observed in combustion of very dry $CO\text{-}O_2$ mixtures which are difficult to ignite and burn slowly, whereas moist mixtures ignite easily and burn rapidly (ref. 1). In the photochemistry of CO_2, the photodecomposition of CO_2 to CO and O is efficient for dry CO_2, but inefficient when traces

of water are present (ref. 2). Evidently, the reverse reaction of CO and O to CO_2 is catalyzed by moisture.

In the absence of hydrogen, the elementary oxidation step must be $CO + O + M \rightarrow CO_2 + M$. From theoretical principles, it is expected that the production of ground state CO_2 by this reaction will be slow, since it requires an electron spin change. The catalytic effect of hydrogen and hydrogen-containing compounds on the oxidation could be due to the reaction $CO + OH \rightarrow CO_2 + H$, where OH has been produced by oxidation of hydrogen compounds. After this reaction, OH could be regenerated by reaction of the atomic hydrogen with atomic oxygen. In contrast to the CO + O reaction, the CO + OH reaction is rapid because spin is conserved. To understand fully the catalytic effect of hydrogen on CO oxidation, accurate rates for both the CO + O and CO + OH reactions are required.

The published results on the rates of CO oxidation by O and by OH differ. No one has measured both reaction rates by the same technique to get reliable relative values of the two. For the CO + O reaction, various workers report results which are in poor agreement (refs. 3 and 4). For the CO + OH reaction, Ashmore (ref. 5) gives the most recent activation energy estimates of 0 to 3 kilocalories per mole (0 to 12.5 kJ/mole) (refs. 6 to 8), while older measurements gave values of 6 to 10 kilocalories per mole (25 to 42 kJ/mole) (refs. 9 to 13). Recently, Dixon-Lewis (ref. 14) using an electron spin resonance technique, reported an OH + CO rate constant value k_{10} of 1.15×10^{11} cubic centimeters per mole per second at 300° K. Herron (ref. 15), using a mass spectrometric technique, reported a k_{10} value of 5.1×10^{10} cubic centimeters per mole per second for the same temperature. These two k_{10} values are actually in much better agreement since the values of the rate constants k_2 for the $OH + OH \rightarrow H_2O + O$ reaction used to derive k_{10} were not the same (private communication from W. E. Wilson, Jr., of Johns Hopkins Univ.). If Herron had used a k_2 value of 1.55×10^{12} cubic centimeters per mole per second (ref. 14) instead of 0.75×10^{12} cubic centimeters per mole per second (ref. 16) his k_{10} value would be 8.6×10^{10} cubic centimeters per mole per second. These values are much higher than previous published results.

The purpose of this report is to provide better rate constants and activation energies for these two reactions. Using the stirred reactor-mass spectrometric technique previously employed by the authors (ref. 17) to study reactions of atomic oxygen, measurements were made at temperatures ranging from 310° to 611° K.

EXPERIMENT AND PROCEDURES

Apparatus

The 300-cubic-centimeter stirred reactor and its connection to the time-of-flight mass spectrometer are shown in figure 1. A more detailed description is presented in

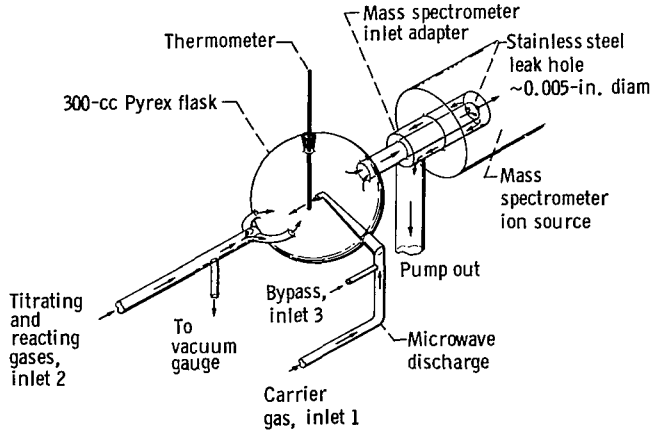


Figure 1. - Stirred reactor and connection to mass spectrometer.

reference 17. The 300-cubic-centimeter reactor was used to study the CO + OH reaction. A larger, 2055-cubic-centimeter, reactor was used for the slow CO + O reaction. Before either reactor was connected to the mass spectrometer, its inside surfaces were wetted with an aqueous 10-percent phosphoric acid solution. The reactor was then dried before being connected to the mass spectrometer to make reaction kinetic measurements. A rhenium filament was used in the ion source to make mass spectrometer measurements because CO could not be monitored when tungsten was the filament wire.

Gases

Carbon monoxide, with a stated minimum purity of 99.5 percent, was sent through a liquid-nitrogen trap before being used. 2.16-Percent H_2 in argon mixture and a 1.46-percent O_2 in Ar mixture were premixed tanked gas mixtures. For both gas mixtures, mass spectrometer analysis showed only trace impurities. Analysis of the 1.46-percent O_2 in Ar mixture showed the presence of 9 ppm H_2O.

Carbon dioxide, with a stated 99.99-percent purity, was used without further purification to calibrate the mass spectrometer for CO_2. Hydrogen gas, with a stated purity of 99.9 percent, was also used without further purification.

Nitrogen dioxide (NO_2) gas for O-atom and H-atom titrations was prepared as needed by adding an excess of O_2 to purified NO. The NO_2 was then condensed out at dry-ice temperature and the excess O_2 removed by vacuum pumping.

Oxygen gas, with a stated purity of 99.5 percent, was sent through two liquid N_2 traps before being subjected to a microwave discharge.

Production of OH Radical for CO + OH Reaction

The hydroxyl radical was produced by the H + NO_2 reaction described in reference 18. Hydrogen atoms were produced by subjecting a 2.16-percent mixture of H_2 in Ar to a microwave discharge. This gas titration reaction was monitored by the mass

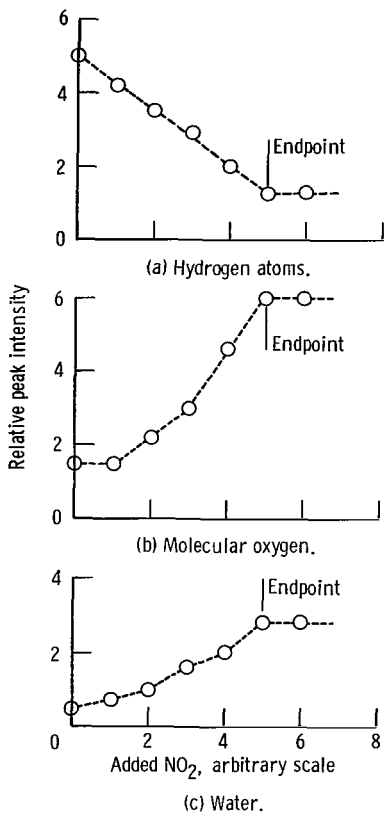


Figure 2. - Mass spectrometer monitoring of endpoint for H + NO_2 titration.

spectrometer. Figure 2 shows a typical gas titration result. End points can be located by monitoring the O_2, H_2O, or H-atom peak. Our mass spectrometer results are consistent with previous findings (refs. 14, 18, and 19) that the reaction scheme for the H + NO_2 reaction at near room temperature is as follows:

$$H + NO_2 \rightarrow OH + NO \quad (1)$$

$$OH + OH \rightarrow H_2O + O \quad (2)$$

$$OH + O \rightarrow O_2 + H \quad (3)$$

Ternary or wall recombination involving these species is too slow to be of importance (refs. 14 and 16). No attempt was made to monitor OH due to its rapid decay (ref. 16). For our experimental condition (2.16-percent H_2-Ar, about 35-percent H_2 dissociated, and a temperature range of 310° to 611° K), the following reaction must be added to the above reaction scheme:

$$OH + H_2 \rightarrow H_2O + H \tag{4}$$

Reaction (4) is relatively unimportant near room temperature but becomes increasingly more important as the temperature is raised.

Production of Oxygen Atoms for CO + O Reaction

In most cases, O atoms for the CO + O reaction were produced by subjecting a 1.46-percent mixture of O_2 in Ar to a microwave discharge. Some runs were also made with O produced by the N + NO titration reaction and by subjecting 100 percent O_2 to a microwave discharge.

Mass spectrometer sensitivity to O was obtained by the usual NO_2 gas titration (ref. 17).

Calculation of Rate Constants

CO + OH reaction. - The bimolecular rate constant k_{10} for the $CO + OH \rightarrow CO_2 + H$ reaction occurring in a stirred reactor is

$$k_{10} = \frac{-\Delta[OH]}{\Delta t[CO]_t[OH]_t} \tag{5}$$

where $-\Delta[OH]$ is the disappearance of OH due to reaction with CO, Δt is residence time, $[CO]_t$ is concentration of CO after reaction with OH, and $[OH]_t$ is concentration of OH after reaction with CO.

Since OH was not monitored, $-\Delta[OH]$ was replaced with its equivalent $+\Delta[CO_2]$, the amount of reaction product produced. The following experimental procedure was used for the rate constant measurement: NO_2 was metered into the reactor through inlet 2 (fig. 1) to titrate H atoms entering the reactor through inlet 1. Then the NO_2 flowrate was adjusted to a point just short of the end point, so that no NO_2 peak could be detected

mass spectrometrically, but only a slight excess of H atoms were present. While this measured NO_2 flow was maintained, CO was then added to the reactor through the same tube. On addition of CO to the reactor, the mass spectrometer indicated that CO_2 and H were produced, and at the same time the H_2O and O_2 concentrations decreased. This observation indicated that the CO + OH reaction is fast enough to compete for the available OH and that the following reactions are occurring in the reactor:

$$H + NO_2 \rightarrow OH + NO \tag{1}$$

$$OH + OH \rightarrow O + H_2O \tag{2}$$

$$OH + O \rightarrow O_2 + H \tag{3}$$

$$OH + H_2 \rightarrow H_2O + H \tag{4}$$

$$CO + OH \rightarrow CO_2 + H \tag{6}$$

From the above reaction scheme, $[OH]_t$ for the stirred reactor in the presence of CO can be calculated. The $[OH]_t$ calculation makes use of an expression which was derived as follows:

$$\text{Total OH decay} = -\frac{d[OH]}{dt} = 2k_2[OH]_t^2 + k_3[OH]_t[O]_t + k_4[OH]_t[H_2]_t + k_{10}[OH]_t[CO]_t \tag{7}$$

By assuming steady-state condition for the oxygen atom, equation (7) is equal to

$$3k_2[OH]_t^2 + k_4[OH]_t[H_2]_t + k_{10}[OH]_t[CO]_t$$

For a stirred reactor,

$$\left.\begin{aligned} -\frac{\Delta[OH]}{\Delta t} &= 3k_2[OH]_t^2 + k_4[OH]_t[H_2]_t + \frac{+\Delta[CO_2]}{\Delta t} \\ -\left(\frac{[OH]_t - [OH]_o}{\Delta t}\right) &= 3k_2[OH]_t^2 + k_4[OH]_t[H_2]_t + \frac{+\Delta[CO_2]}{\Delta t} \end{aligned}\right\} \tag{8}$$

Equation (8) can be solved for $[OH]_t$ such that

$$[OH]_t = \frac{-\left\{\left(k_4[H_2]_t\,\Delta t\right)+1\right\}+\sqrt{\left\{\left(k_4[H_2]_t\,\Delta t\right)+1\right\}^2+12k_2\,\Delta t\left([OH]_0-[CO_2]_t\right)}}{6k_2\,\Delta t} \tag{9}$$

where $[CO_2]_t$ is the concentration of CO_2 produced in reaction (6) and is equal to $+\Delta[CO_2]$, k_2 and k_4 values are given in references 14 and 16, $[OH]_0$ is the total initial OH concentration and is equal to $[NO_2]_0$, and Δt and H_2 are known.

The rate constant $k_{10,\,CO_2}$ for reaction (6) based on CO_2 production can now be evaluated by the equation

$$k_{10,\,CO_2} = \frac{+\Delta[CO_2]}{\Delta t[CO]_t[OH]_t} \tag{10}$$

An alternate method to calculate k_{10} is based on the observation that each time more CO is added, the increase in CO_2 production is accompanied by a simultaneous decrease in water production, designated as $-\Delta[H_2O]$. This second phenomenon must be due to the competition between reactions (2), (4), and (6) to consume the available OH and is a comparison of the rates of reactions (2) and (4) to reaction (6). This relation can be expressed by the equation

$$\frac{k_{10}[CO]_t[OH]_t}{k_2[OH]_t^2+k_4[OH]_t[H_2]_t}=\frac{[CO_2]_t}{[H_2O]_t} \tag{11}$$

Equation (11) can be rewritten using the term R, which is the ratio of $k_4[H_2]_t$ to $k_2[OH]_t$.

$$\frac{k_{10}[CO]_t}{k_2[OH]_t(1+R)}=\frac{[CO_2]_t}{[H_2O]_t} \tag{12}$$

The term $[CO_2]_t$ can be expressed in terms of the $-\Delta[H_2O]$ since, for each mole of H_2O removed, B moles of CO_2 can be produced, where B is a function of R. For the case

where R is equal to 0, B = 2, and where R is ∞, B = 1. Equation (12) can now be rewritten as

$$\frac{k_{10}[CO]_t}{k_2[OH]_t(1 + R)} = \frac{-B\Delta[H_2O]}{[H_2O]_t} \tag{13}$$

and an alternate rate constant for the CO + OH reaction designated as k_{10, H_2O} can also be calculated since $-\Delta[H_2O]/[H_2O]_t$ was measured mass spectrometrically and all other terms are known or can be evaluated.

CO + O Reaction. - The termolecular rate constant for the reaction CO + O + M → CO_2 + M occurring in the stirred reactor is

$$k_{14} = \frac{-\Delta[O]}{\Delta t[CO]_t[O]_t[M]} \tag{14}$$

where $-\Delta[O]$ is the decay of O atoms, $[O]_t$ is the O concentration in the reactor after reaction with CO, and [M] is the total gas concentration in moles per cubic centimeter.

This reaction is so slow that the O decay was less than experimental error. However, the production of CO_2 could be measured, due to the lack of CO_2 background ion current. Consequently, the rate constant k_{14} was estimated by substituting $+\Delta[CO_2]$ for $-\Delta[O]$ in equation (14).

RESULTS AND DISCUSSION

Rate Constants for CO + OH Reaction

When CO and NO_2 are added through a common tube to H in a reactor as described in the previous section, significant amounts of CO_2 are produced and can be measured mass spectrometrically. The CO_2 production for increasing amounts of added CO, expressed as the mole fraction F_{CO}/F_t, where F_{CO} and F_t are CO and total gas flow rates, respectively, at a temperature of 310° K is shown in figure 3(a). The carbon dioxide yield falls off as F_{CO}/F_t is increased, and the CO_2 production expressed in cubic centimeters per second (NTP) is independent of temperature (table I). Occurring simultaneously with CO_2 production is the decrease in the amount of water due to the competition of reaction (6) with reactions (2) and (4). This effect was also measured mass spectrometrically, and the data for 310° K is shown in figure 3(b) as a plot of the fraction of H_2O removed

TABLE I. - RATE MEASUREMENTS DATA FOR CARBON MONOXIDE WITH HYDROXYL RADICAL REACTION

[Dilute hydrogen-argon flow (NTP), 1.50 cm^3/sec.]

Run	Added carbon monoxide flow (NTP)[a], $(F_{CO})_O$, cm^3/sec	Mole fraction of added carbon monoxide, F_{CO}/F_t	Temperature, ^oK	Added nitrogen dioxide flow (NTP)[a], $(F_{NO_2})_O$, cm^3/sec	Pressure, P		Residence time, Δt, sec	Reaction product CO_2 flow (NTP)[a], $(F_{\Delta CO_2})$, cm^3/sec	Calculated flow of OH (NTP)[a], $(F_{OH})_t$, cm^3/sec	Fraction of H_2O removed, $\frac{-\Delta[H_2O]}{[H_2O]_O}$	Moles of water removed per mole of carbon dioxide produced, B (b)	Rate constant, k_{10, CO_2}, $cm^3\,mole^{-1}\,sec^{-1}$	Rate constant, k_{10, H_2O}, $cm^3\,mole^{-1}\,sec^{-1}$
					mm	N/m^2							
1a	0.0289	0.0186	310	0.0240	0.70	93	0.173	0.0051	0.93×10^{-3}	0.24	1.93	5.7×10^{10}	4.3×10^{10}
b	.0609	.0385			.70	93	.169	.0084	.86	.36	1.93	4.9	3.2
c	.0993	.0613			.71	94	.167	.0107	.80	.43	1.92	4.0	2.4
d	.1520	.0910			.72	96	.165	.0132	.73	.49	1.92	3.5	1.8
2a	.0238	.0154	311	.0245	.70	93	.172	.0040	.98	.23	1.93	5.2	5.1
b	.0477	.0302			.70	93	.169	.0068	.92	.40	1.93	4.7	5.2
c	.0765	.0475			.71	94	.168	.0095	.85	.49	1.92	4.4	4.2
d	.1226	.0743			.72	96	.166	.0112	.81	.55	1.92	3.3	3.1
e	.1737	.1022			.73	97	.163	.0129	.76	.62	1.92	2.9	2.7
3a	.0232	.0151	444	.0215	.70	93	.121	.0037	.94	.20	1.63	10.2	8.2
b	.0486	.0310	443		.70	93	.120	.0068	.84	.30	1.61	10.0	6.2
c	.0708	.0445	442		.71	94	-----	.0090	.77	.44	1.58	9.9	7.4
d	.1066	.0658	441		.71	94	.118	.0113	.70	.53	1.56	9.0	6.2
e	.1475	.0868	---		.73	97	.115	.0134	.61	.58	1.52	9.1	5.0
4a	.0307	.0198	438		.70	93	.122	.0045	.91	.26	1.64	9.4	8.3
b	.0409	.0262	437		.70	93	-----	.0064	.86	.39	1.63	10.8	10.8
c	.0698	.0439	436		.71	94	.121	.0086	.79	.47	1.61	9.0	8.1
d	.0936	.0581	436		.71	94	.120	.0105	.73	.59	1.58	8.9	9.1
e	.1315	.0791	436		.72	96	.118	.0119	.68	.60	1.56	7.7	6.2
5a	.0193	.0125	606	.0244	.70	93	.089	.0028	1.07	.09	1.41	14.6	8.0
b	.0403	.0258	607		.70	93	.088	.0052	1.00	.14	1.38	14.2	5.9
c	.0613	.0388	608		.71	94	-----	.0074	.93	.24	1.36	14.4	7.6
d	.0993	.0613	---		.71	94	.085	.0104	.83	.40	1.33	14.2	9.2
e	.1280	.0776	610		.72	96	.085	.0122	.76	.49	1.28	14.3	9.2
f	.1727	.1022	---		.72	96	.083	.0140	.70	.58	1.28	13.6	9.9
h	.0334	.0215	610	.0244	.70	93	.088	.0048	1.02	.21	1.39	15.0	12.0
6a	.0559	.0354	611		.70	93	.086	.0074	.95	.31	1.36	16.1	11.7
b	.0829	.0518			.70	93	.085	.0095	.87	.42	1.34	15.2	12.1
c	.1159	.0707			.72	96	.085	.0113	.80	.54	1.32	13.8	12.8
d	.1552	.0924			.72	96	.083	.0133	.73	.61	1.29	13.7	12.9

[a]Normal temperature (300° K) and pressure (750 mm) (100 000 newtons/meter^2).

[b]B is a function of the ratio of $[k_4\,H_2]$ and $[k_2\,OH]_t$.

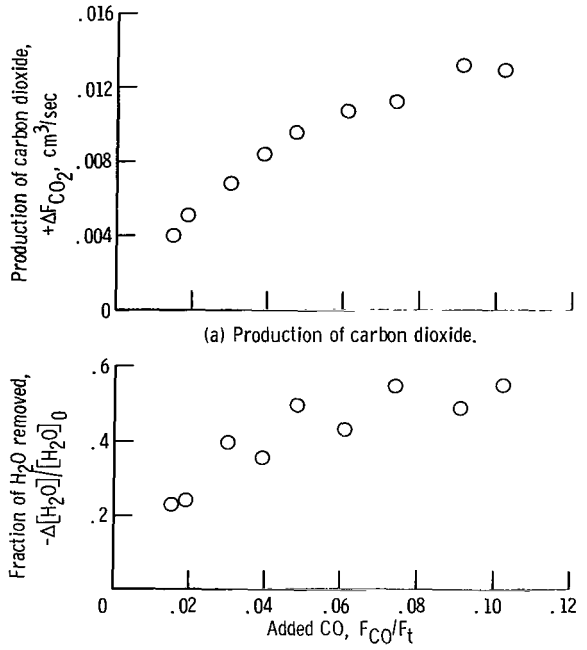


Figure 3. - Fraction of CO + OH reaction at 310° K.

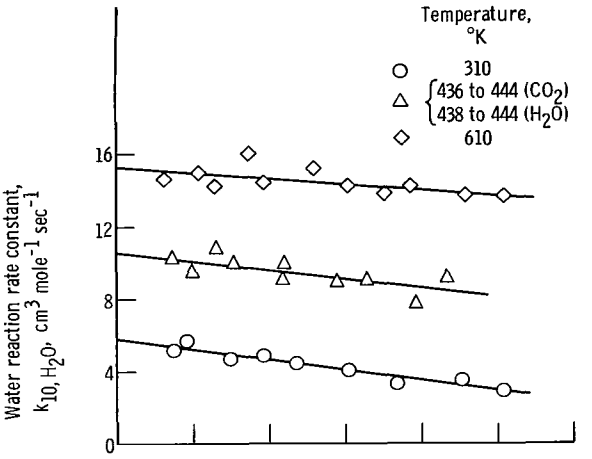
$-\Delta[H_2O]/[H_2O]_0$ against F_{CO}/F_t where $-\Delta[H_2O]$ is the moles of water removed after addition of CO, and $[H_2O]_0$ is the initial amount of H_2O present before addition of CO. Although the scatter for this water data is considerable, a similar trend, as for the CO_2 production, was noted. Both sets of data are listed in table I.

The data shown in figure 3 can now be used in equations (10) and (13) to evaluate rate constants k_{10, CO_2} and k_{10, H_2O}. The results of these calculations are tabulated in table I and shown in figure 4 as plots of rate constant against F_{CO}/F_t. In figure 4(a), the k_{10, CO_2} trend with F_{CO}/F_t at three different temperatures is fairly well established. The k_{10, H_2O} trends with F_{CO}/F_t shown in figure 4(b) can only be determined for the two lower temperatures because the k_{10, H_2O} values at the highest temperature scatter considerably.

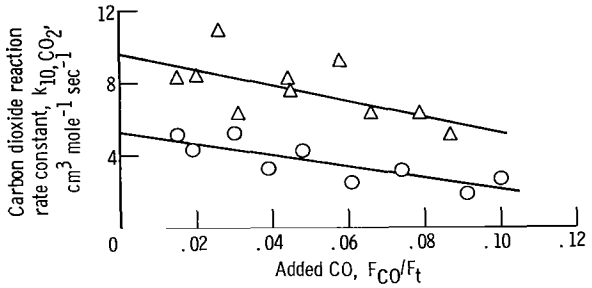
These k_{10} rate constant trends with F_{CO}/F_t may be explained by the fact that both $+\Delta[CO_2]$ and $-\Delta[H_2O]/[H_2O]_0$ tend to level out as F_{CO}/F_t is increased and the lack of available OH becomes a limiting factor.

The k_{10, CO_2} and k_{10, H_2O} values for the various temperatures were obtained by drawing least squares lines through the appropriate data shown in figure 4. Rate constant values independent of F_{CO}/F_t can thus be determined and are tabulated as follows:

Temperature, T, °K	Rate constant, cm^3 $mole^{-1}$ sec^{-1}	
	k_{10, CO_2}	k_{10, H_2O}
~310	5.8×10^{10}	5.3×10^{10}
~440	10.6	9.6
~610	15.3	--------



(a) Reaction rate constant for CO_2.



(b) Reaction rate constant for H_2O.

Figure 4. - Rate constants variations with added CO.

The k_{10, CO_2} values for the three temperatures were estimated to have a precision of at least ±10 percent, because all the k_{10, CO_2} data (fig. 4(a)) deviated ±10 percent or less from their respective least squares lines. The two k_{10, H_2O} values had much poorer precision of about ±20 percent. There is good agreement in the k_{10} values for the two lower temperatures.

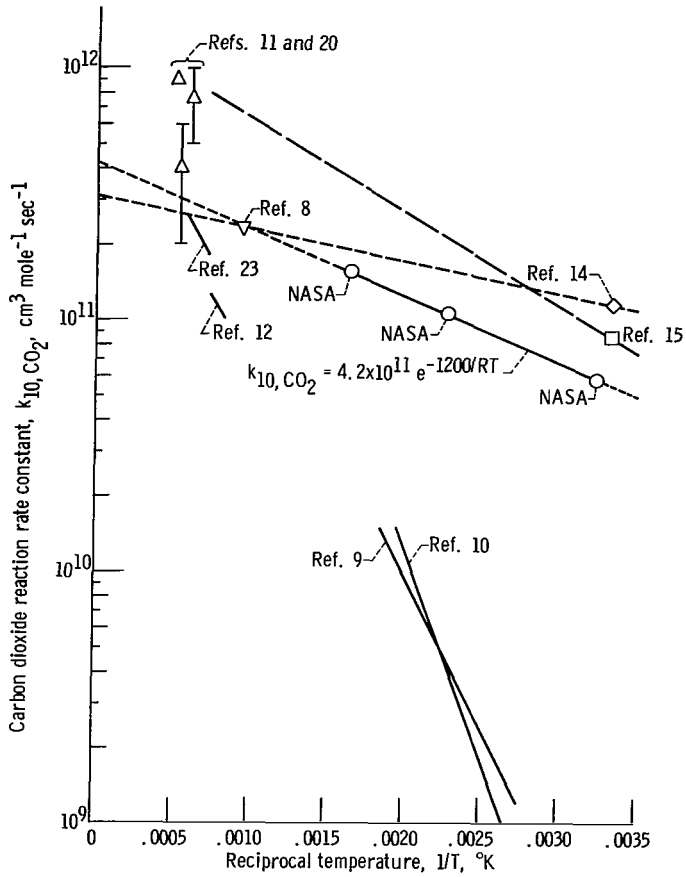


Figure 5. - Comparisons of rate constants for the CO + OH reaction.

Using the k_{10, CO_2} values tabulated above, an Arrhenius plot of k_{10, CO_2} against the reciprocal of the absolute temperature is made (fig. 5), and the rate constant k_{10} for the CO + OH reaction is equal to $(4.2 \pm 0.8) \times 10^{11} \exp(-1200 \pm 300/RT)$ cubic centimeters per mole per second, where R is the gas constant and T is the absolute temperature. We estimate that our preexponential term has a ±20 percent error and that ΔE, the activation energy, has about a ±25 percent error.

Comparisons of Rate Constant Measurements for CO + OH Reaction

Rate constant values for the CO + OH reaction obtained by various investigators are also shown in figure 5. The low-temperature data were all from flow discharge experiments using tube reactors, and high-temperature data were mostly from flame studies. The recent low-temperature measurements of references 14 and 15 and the results pre-

sented herein suggest that Avramenko's results are questionable due to the use of a water discharge as an OH source (ref. 16). At 300° K our k_{10} value of 5.4×10^{10} cubic centimeters per mole per second are lower than Herron's recalculated value of 8.6×10^{10} (ref. 15) and Dixon-Lewis and Westenberg's value of 1.5×10^{11} (ref. 14). The low k_{10} value reported herein may be due to incomplete mixing in the reactor because of the very rapid reactions. It is interesting to assume that, in the reactor, very little mixing is occurring, and treat the data for 300° K using an unstirred reactor concept. To make this calculation, an integrated expression for a tube reactor (ref. 15) is used.

$$k_{10} = \frac{+\Delta[CO_2]}{[CO]\int_0^t [OH]\,dt} \tag{15}$$

Equation (15) was integrated using an expression for the OH decay which omitted the additional OH loss due to the CO + OH reaction.

$$k_{10} \approx \frac{1.3\,\Delta[CO_2]}{[CO]} \frac{k_2}{\mathrm{Log}\left(3k_2[OH]_0\,\Delta t + 1\right)} \tag{16}$$

Using the above equation, a k_{10} value of $\approx 1.3\times10^{11}$ cubic centimeters per mole per second was obtained. This value would be higher if a more exact expression for the OH decay had been used in equation (16). The fact that our two k_{10} values (calculated using a stirred reactor and an unstirred reactor concept) bracketed the other two recently reported k_{10} values suggests that the reactor reported herein had incomplete mixing.

The ΔE estimate of 1200 calories per mole (5000 J/mole) can be compared with two recent ΔE estimates of 600 and 1700 calories per mole (2500 and 7100 J/mole) (refs. 14 and 15, respectively) for this reaction. These referenced values were both obtained by combining measured k_{10} values at 300° K with some other k_{10} values obtained by workers using flame studies at the higher temperatures.

The possibility that some of the CO_2 produced in the CO + OH experiment was due to the action of HO_2, the hydroperoxy radical, was eliminated by reacting H with a mixture of O_2 + CO instead of NO_2 + CO. Only a minor amount of CO_2 was produced for our experimental condition. An approximate rate for the CO + HO_2 reaction at room temperature can be obtained by making a crude estimate that the $+\Delta[CO]_2$ was only about 1/50 of the $+\Delta[CO_2]$ for the CO + OH reaction and that the $[HO_2]_t$ in the stirred reactor was about the same as $[OH]_t$ in the previous experiments. Then the rate for the CO + HO_2 reaction is about 10^8 to 10^9 cubic centimeters per mole per second.

Rate Constants for CO + O Reaction

Most of the measurements for this reaction were conducted using a 2055-cubic-centimeter reactor and atomic oxygen derived from a 1.46-percent O_2-Ar gas mixture. For a temperature range of 400° to 500° K, pressures of 0.75 to 3.5 millimeters (100 to 465 N/m^2), and amounts of added CO to a mole fraction of 0.15, the loss of atomic oxygen due to reaction with CO was too small to be detected. Traces of CO_2 were observed at the lower limit of detection of the mass spectrometer. It was estimated that the mole fraction of CO_2 produced was about $\leq 10^{-3}$ at 500° K. Similar results were obtained using atomic oxygen from the N + NO titration technique and from discharged 100-percent O_2.

The reaction of CO and O is expected to occur primarily by a termolecular process, with a third body required to carry away the heat of reaction. This is contrary to the results of Mahan and Solo (ref. 4) who found the reaction to be apparently bimolecular. In spite of their results, because of the strong theoretical expectation that the reaction is termolecular, the rate constant reported herein has been calculated for a termolecular reaction. For this calculation, the upper limit mole fraction value of 10^{-3} for CO_2 production, the observed oxygen atom mole fraction value of 0.014, Δt = 1 second, the added CO mole fraction value of 0.15, and a total pressure of 1 millimeter (133 N/m^2) were used. The rate constant that resulted was 4×10^{13} cubic centimeters squared per mole squared per second. This value represents an upper limit, because of uncertainty in estimating the background ion current for CO_2. Other rate constants from the literature are listed for comparison in table II. The bimolecular rate constant of Mahan and Solo (ref. 4) has been recalculated as a termolecular rate constant at a total pressure of 1 millimeter (133 newtons/meter^2) to allow a direct comparison with the termolecular rate constants

TABLE II. - RATE CONSTANTS FOR CARBON MONOXIDE PLUS OXYGEN ATOM REACTIONS

Investigator	Rate constant, k, $cm^6\ mole^{-2}\ sec^{-1}$	Temperature, $^{\circ}K$
Mahan and Solo[a], 1962 (ref. 4)	7×10^{15}	500
Avramenko and Kolesnikova, 1959 (ref. 3)	8×10^{16}	500
Kaufman, 1961 (ref. 24)	$<5 \times 10^{14}$	300
Clyne and Thrush, 1963 (ref. 25)	$<3 \times 10^{13}$	300
Groth[b], 1937 (ref. 26)	1×10^{13}	300
Kondrat'ev and Ptichkin, 1961 (ref. 27)	5×10^{13}	500
Brabbs and Belles, 1966 (ref. 28)	2×10^{13}	3000
This research, 1967	$\leq 4 \times 10^{13}$	500

[a]Reported reaction to be bimolecular.

[b]Relative rate to $O + O_2 + M - O_3 + M$.

reported by others. Large differences are evident in table II, with rate constants ranging from 10^{13} to 10^{16} cubic centimeters squared per mole squared per second. The general weight of the results favor a low value, less than about 5×10^{13} cubic centimeters squared per mole squared per second.

Effect of Traces of Hydrogen Compounds on CO + O Reaction

The large differences between different measurements of the CO + O rate constant are outside experimental error. We believe that this might be due to hydrogen compounds in the system, resulting in the presence of OH Since OH reacts so rapidly with CO, traces of this compound will greatly affect the oxidation rate of CO. Using the rate constants obtained in the present investigation shows that, at 500° K and a pressure of 1 millimeter (133 N/m^2), the rate of CO_2 formation by O and OH are equal when the ratio of [O] to [OH] is 10^5. Thus, for experimental conditions, where the atomic oxygen mole fraction is usually about 0.014, a mole fraction of OH larger than 1×10^{-7} could result in most of the CO_2 being due to the CO + OH reaction. This indicates how difficult it is to make reliable CO + O rate measurements, unless extreme care is used to remove traces of moisture or other hydrogen compounds from the system. Moisture in the oxygen will yield OH when the mixture is passed through the discharge. Hydrogen or hydrocarbons in the CO will yield OH by reaction with atomic oxygen. In either case, it seems possible that none of the rate constants reported for the CO + O oxidation are correct. All observed CO_2 formation may be due to the presence of traces of OH. In order to gain some experimental evidence of the importance of moisture, the O_2-Ar mixture was bubbled through water at room temperature at 1 atmosphere pressure (1×10^5 N/m^2) before being passed through the microwave discharge. The amount of CO_2 produced upon reaction with CO in the reactor was doubled for this "wet" mixture. Evidently, OH was present in large enough amounts to influence considerably the reaction rate.

The rate constant reported by Mahan (ref. 4) is about 100 times larger than the observations reported herein, possibly indicating the presence of OH in Mahan's system. Evidence for this can be seen from some of Mahan's experiments in which NO_2 was introduced into the reactor with CO and O. The addition of NO_2 increased the CO_2 production by a factor of about nine. This large effect might be due to the CO + OH reaction, in which the OH was generated by a cyclic process involving the reaction of H + NO_2 → OH + NO, followed by reaction of OH with CO to form CO_2 and H. The phenomenon of an increase in CO_2 production when NO_2 is added to a CO + O system was also observed recently by Harteck, Reeves, and Thompson (ref. 21). The fact that Mahan observed a bimolecular rate constant might also arise from the dominance by OH of the oxidation process.

SUMMARY OF RESULTS

Rate measurements were made on the CO + OH and CO + O reactions with the following results:

1. For the CO + OH → CO_2 + H reaction the rate constant k_{10} based on CO_2 production was determined to be $(4.2\pm0.8)\times10^{11}\exp(-1200\pm200/RT)$ cubic centimeters per mole per second. The rate constant value at 300° K is somewhat lower than two recent measurements of this value possibly because the reactor was not completely mixed. The measured ΔE of 1200 calories per mole (5000 J/mole) agrees with the more recent ΔE estimates of 0 to 2000 calories per mole (0 to 8333 J/mole) for this reaction.

2. For the CO + O + M → CO_2 + M reaction, an upper limit estimate of its rate constant at 500° K was found to be 4×10^{13} cubic centimeters squared per mole squared per second. This value agrees approximately with some published results, but is much smaller than other published rate constant values. The wide scatter in published rate constant values is believed due to the presence of hydrogen compounds in the various experimenters' reaction systems.

Lewis Research Center,
National Aeronautics and Space Administration,
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